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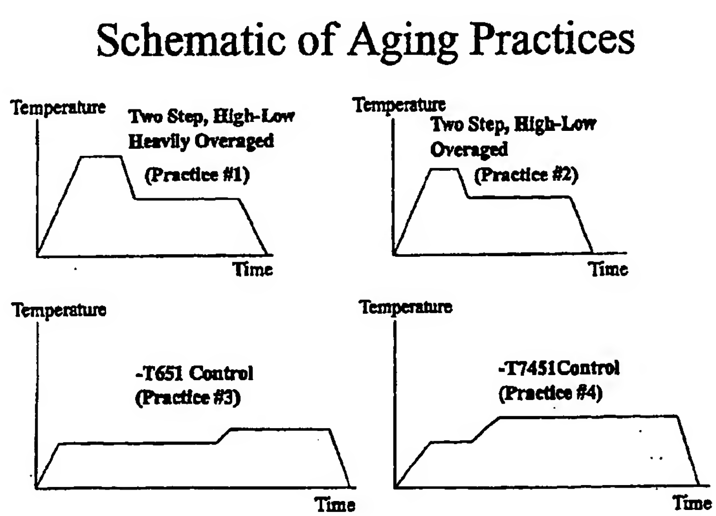

(57) Abstract

A method for the heat treatment of thick 7000 series aluminum alloy products which results in superb corrosion resistance and strength is disclosed. The inventive method consists of processing a 7000 series aluminum alloy to a semi-finished product in the quenched (-W) condition and then aging by: controlled heating to a high elevated temperature (from about 335 degrees to 450 degrees F); holding at this elevated temperature; cooling to a lower elevated temperature (from about 235 degrees to 310 degrees F); holding at this lower elevated temperature; and finally cooling to room temperature. The resulting product has exfoliation and stress corrosion resistance vastly superior to -T6X tempered products at strength levels much greater than conventional -T7X tempered products. The figure is a schematic illustration of the thermal history for prior art aging practices and aging practices in accordance with the present invention.

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HEAT TREATMENT FOR THICK ALUMINUM PLATE

FIELD OF THE INVENTION

The present invention relates to an improved AA7000 series aluminum plate product and a process for producing the product. The product has improved combinations of strength, exfoliation corrosion resistance and stress corrosion cracking resistance.

BACKGROUND OF THE INVENTION

Aluminum alloys of the Aluminum Association ("AA") 7000 series which contain high amounts of zinc, magnesium, and copper are used extensively in commercial and military aircraft applications. These alloys have very high strength-to-weight ratios and are therefore used in critical load-bearing structural components such as wings and bulkheads. However, in these applications they are subjected to environments which can promote severe corrosion. Moist, hot, seacoast exposure which is present in tropical regions, is particularly detrimental and can promote severe exfoliation and stress corrosion of the metal. Therefore, what is desired is a 7000 series aluminum material which possesses high strength and corrosion resistance.

There are two approaches to improving the corrosion resistance of 7000 series aluminum alloys. The first is to slightly modify the chemical composition of the alloy. This approach is effective to an extent as shown by Staley et al. in U.S. Patent Number 3,881,966. However,

by far the more explored approach is the method by which a set composition is thermally aged following solution heat treatment and quenching. It is this second approach, the method of aging, which involves the present invention.

One of the traditional methods of aging a 7000 series alloy, such as AA7150, as described in United States Patent No. 4,305,763 to Quist and Hyatt, is to age at a low elevated temperature followed by a higher elevated temperature until the alloy reaches its maximum possible or peak strength. This low-temperature, high-temperature age practice which results in peak strength is commonly designated the -T651 temper. The metallurgical objective of this practice is to carefully form a stable distribution of G.P. zone clusters and fine $MgZn_2$ type transitional precipitates during the first lower elevated temperature step. The second higher elevated temperature step then coarsens the fine stable precipitate distribution until a size is reached which most effectively inhibits dislocation motion, thereby resulting in peak strength. Although this age practice results in high strength and good mechanical properties, typically ~82 ksi yield strength for 7X50 alloys, it also produces poor corrosion resistance. Typical exfoliation corrosion resistance resulting from this age practice is an EC to ED rating as measured by ASTM G34 testing methods. Stress corrosion is also quite poor at a short transverse stress corrosion threshold of 7 ksi when tested by alternate immersion in 3.5% NaCl solution per ASTM G49 and G44 testing methods.

Ponchel et al., in U.S. Patent Nos. 4,828,631 and 4,954,188, describe a single-step low elevated temperature aging practice to improve the exfoliation resistance of 7000 series alloys without decreasing strength. Ponchel's age practice involves aging within

a temperature range from about 265°F to 290°F for about 6 to 60 hours to a peak strength condition, which is commonly designated the -T6151 temper. Metallurgically, this practice results in less precipitation of alloying elements from solid solution compared to the Quist and Hyatt practice and consequently improves exfoliation resistance to typically the EB level as measured by ASTM G34 testing methods. Although Ponchel's development improves exfoliation resistance, it unfortunately does not improve stress corrosion cracking resistance. Short transverse stress corrosion resistance is still quite poor with a stress corrosion threshold of 7 ksi.

Faced with the problem of very severe stress corrosion resulting from both the Quist and Hyatt, and Ponchel et al. peak strength age practices, many users of 7000 series aluminum alloys decided to utilize lower strength but improved stress and exfoliation corrosion resistant conventional -T7 type tempers. These -T7X tempers are termed to be overaged in that during aging the precipitates are coarsened past or over the size which is optimum for inhibiting dislocation motion. This "overaging" decreases strength significantly compared to the optimum precipitate size distribution which occurs at peak strength but has the advantage of markedly improving exfoliation and stress corrosion properties. For example, for 7X50 type alloys these -T7 temper practices sacrifice ~11 to 14 ksi in lower yield strength to dramatically improve stress and exfoliation resistance as compared to peak strength tempers. The exfoliation resistance of -T7X tempers is typically EA and the short transverse stress corrosion threshold is increased to a minimum of 25 and more typically 35 ksi. One of the oldest methods by which to achieve a -T7X temper and improve intergranular corrosion resistance in 2XXX and 7XXX alloys is described by Sublett and Fien in U.S.

Patent 3,305,410. Sublett and Fien's practice involves aging at high elevated temperature for a portion of the total aging time followed by aging at lower elevated temperature for a longer portion of the total aging time. This practice should also improve stress corrosion resistance. In actual modern day production practice, a -T7X temper is achieved by using a Quist and Hyatt low-temperature, then high-temperature aging approach, with the exception of significantly extending the amount of time at the second high temperature to overage the precipitate distribution.

The commercial potential of these -T7X tempers is significant. No applications are known where any temper is used other than -T7X tempers when product thicknesses are 3.00" and over. It is typically in these thicker gauges of ~1.00" and above where short transverse stress corrosion is of substantial concern.

In an effort to improve upon the classic strength/corrosion tradeoff associated with 7XXX series aluminum alloys just described, a process has been developed for producing tempers referred to as three-step retrogression and re-aging (RRA) tempers. The inventor of this concept was Cina et al., as described in U.S. Patent No. 3,856,584. The RRA concept metallurgically involves three essential aging steps as described by Liu et al. in U.S. Patent No. 5,108,520. The first aging step occurs at a low elevated temperature specifically for carefully forming a stable distribution of G.P. Zone clusters and fine $MgZn_2$ type transitional precipitates, which is actually identical to the first step of the age practice developed by Quist and Hyatt. Brown et al., in U.S. Patent No. 4,863,528, provides insight into Cina's process by noting the level of strengthening required in this step should be to a level exceeding as-solution heat treated strength by at least about 30% of the difference

between as-solution heat treated strength and peak strength.

Unlike Quist and Hyatt, the second step involves a very rapid heating to a significantly higher elevated temperature. The purpose of this very rapid heating is to revert or dissolve into solid solution a substantial number of the precipitates which were formed during the first aging step. It is this second very rapid heating step which improves the exfoliation and stress corrosion resistance of this material compared to -T6X tempers. The best insight into the rate of heating required for this reversion is given by Dubost et al. in U.S. Patent Nos. 4,189,334 and 4,200,476. Dubost explains a rate higher than 1°C/minute from 150°C to 190°C is necessary (above ~108°F/hr). Brown mentions rapid heating by immersion in molten salt, hot oil, molten metal, hot air, and particularly a fluidized bed, all of which are faster than the 1°C/minute of Dubost. The underlying metallurgical mechanism of why this rapid heating promotes corrosion resistance is not understood at this time. There are many theories present in the literature, some of which involve microchemistry differences near grain boundaries and partitioning of solute to large grain boundary precipitates.

The second step rapid heating to a significantly higher elevated temperature, as mentioned, dissolves many of the precipitates which actually strengthen the material. This necessitates the third and final aging step. The third aging step involves a low elevated temperature age, often the same or similar to the first step, solely for the purpose of restrengthening the material. The precipitate size distribution desired is that which most effectively inhibits dislocation motion and results in near peak strength. This three-step RRA-type processing for 7X50 type alloys results in a

sacrifice of ~1 to 2 ksi in yield strength for the purpose of increasing exfoliation resistance to typically an EA or EB rating and short transverse stress corrosion to a threshold value of 25 ksi as compared to -T6X type tempers. This three-step processing, unfortunately, does not result in the degree of corrosion resistance that the most widely used -T7X tempers afford.

One of the primary limitations of the three-step RRA practice is the rapid heating rate required in the second age step. A negative consequence of requiring a rapid heat-up is the limitations inherently placed on the thickness of the material being aged. The inventor of the three-step RRA concept, Cina, practiced his invention primarily on thin sheet materials. Unfortunately, this processing was not very widely utilized because in thin materials stresses are in-plane and not in the short transverse through-thickness direction where the susceptibility to stress corrosion is most severe. Basic heat transfer equations make it difficult, if not impossible, to rapidly heat a thick mass very uniformly to an elevated temperature. The through-thickness differences in temperature are quite severe and can result in non-uniform properties. Dubost's process, even with heating rates down to a minimum of about 108°F/hr, required that his products be immediately cooled without holding isothermally at the highest maximum aging temperature. This obviously requires, from a commercial viewpoint, extreme furnace temperature controls. Additionally, by changing immediately from rapid heating to cooling, the thick section will not see uniform through-thickness temperature. Consequently, properties will not be uniform throughout the cross-section. Brown and Liu's three-step RRA aging practices somewhat overcome the deficiencies of Dubost's development;

however, like Dubost, they still inherently utilize a fast heating rate in the second aging step.

From an economic standpoint, three-step RRA practices are additionally very expensive. State-of-the-art furnaces with tremendous heat input and precise temperature control are desired to perform rapid, accurate heating and/or cooling for the second step age. Alternatives to these furnaces are even more expensive heat treating equipment such as fluidized beds, as mentioned by Brown. From every apparent aspect, large capital expenditures are required for utilizing this three-step aging method. Even if this large capital expenditure is made, the resulting corrosion properties will not equal the more widely used -T7X tempers and this age process is of very limited utility in aging thick products or even large coils of thin sheet.

SUMMARY OF THE INVENTION

Quite unexpectedly, it has been discovered that very high strength and excellent exfoliation and stress corrosion resistance can be achieved in AA7000 series aluminum alloy thick plate by using two-step high temperature-low temperature aging practices which utilize heating rates which are commonplace in standard aluminum metallurgical production. This contrasts quite starkly with the teachings of the prior art. The teachings of Sublett and Fien show that intergranular corrosion resistance can be improved but with a commensurate loss of strength which is typical of a -T7 overaging practice. Both Quist's and Hyatt's -T651 age practice and conventional -T7X overaged practices utilize low temperature-high temperature aging, which is exactly the opposite of the inventive method. In contrast to three-step RRA-type temper aging practices, the commonplace heating rates used in this two-step practice make it

possible to easily and much more cost effectively age 7000 series alloy thick plate to a high strength, with improved combinations of exfoliation and stress corrosion resistance properties.

Thus, in accordance with a preferred embodiment of the invention, 7000 series aluminum base alloy products with improved combinations of high strength and exfoliation and stress corrosion resistance are obtained. Examples of alloys that can be processed with the process provided by the present invention include alloys with the following elemental composition: from about 5.0 to 10.0 wt. % zinc, from about 1.6 to 3.2 wt. % magnesium, from about 1.0 to 3.0 wt. % copper, from about 0 to 0.15 wt. % zirconium, from about 0 to 0.3 wt. % of at least one grain refining element, such as but not limited to titanium, boron, chromium, and hafnium, less than about 0.5 wt. % Fe, Si and other impurity elements, with the balance being aluminum. The alloy product is subjected to hot working, solution heat treating, and quenching, followed by a two-step aging process according to the present invention. The aging process consists of heating the product from room temperature at a rate less than about 100°F/hr to a first high elevated temperature in the range of about 335°F to 450°F, holding the product at one or more temperatures within the first range for a time of about 0.25 to about 6 hours, followed by holding the product at one or more temperatures within a second lower elevated temperature range of about 235°F to about 310°F for a time of about 3 to 60 hours. The product can be cooled directly from the first range to the second range or can be cooled from the first range to ambient and then re-heated to the second range.

An object of the present invention is to provide a relatively thick aluminum alloy plate product having improved combinations of strength, exfoliation corrosion

resistance, and stress corrosion cracking resistance. Another object is to provide a process for producing a thick aluminum alloy plate product having an improved combination of properties. Other objects and advantages of the present invention will become apparent as the description thereof proceeds.

BRIEF DESCRIPTION OF THE DRAWINGS

Further features, other objects and advantages of the present invention will become apparent from the following detailed description of preferred embodiments, in conjunction with the drawings, in which:

Figure 1 is a schematic illustration of the thermal history for prior art aging practices and aging practices in accordance with the present invention.

Figure 2 is a graph of strength vs toughness for two products aged by the inventive method and products aged to the -T7451 and -T651 condition.

Figure 3 is a 7X50 iso-property map for tensile yield strength from Example 2.

Figure 4 is a 7X50 iso-property map for ultimate tensile strength from Example 2.

Figure 5 is a 7X50 iso-property map for % tensile elongation from Example 2.

Figure 6 is a 7X50 iso-property map for short transverse stress corrosion at 25 ksi from Example 2.

Figure 7 is a 7X50 iso-property map for short transverse stress corrosion at 35 ksi from Example 2.

Figure 8 is a 7X50 iso-property map for exfoliation corrosion resistance by ASTM G34-79 at the t/10 thickness plane from Example 2.

Figure 9 is a 7X50 iso-property map for exfoliation corrosion resistance by ASTM G34-72 at the t/10 thickness plane from Example 2.

Figure 10 is a 7X50 iso-property map for exfoliation corrosion resistance by ASTM G34-79 at the t/2 thickness plane from Example 2.

Figure 11 is a 7X50 iso-property map for exfoliation corrosion resistance by ASTM G34-72 at the t/2 thickness plane from Example 2.

Figure 12 is a 7X50 iso-property map for exfoliation corrosion weight loss at the t/10 thickness plane from Example 2.

Figure 13 is a 7X50 iso-property map for exfoliation corrosion weight loss at the t/2 thickness plane from Example 2.

Figure 14 is an example of superimposing two different iso-property maps in order to select an age practice which will result in desired material properties.

Detailed Description of the Preferred Embodiments

The present invention is directed to an improved AA7000 series thick plate product having a superior combination of properties and a process for producing such product.

One of the objects of the invention is to provide a two-step aging practice which results in improved combinations of high strength, exfoliation corrosion resistance and stress-corrosion resistance in thick aluminum alloy plate products of the AA7000 series. Another object of the invention is to provide a practice useful with thick product forms, such as plate, extrusions and forgings. Yet another object of the invention is to provide a relatively economical, cost effective practice that is easy to implement in terms of process control for a typical commercial aluminum production facility. With these objectives in mind, a

detailed description of preferred embodiments of this invention follows.

The inventive two-step aging method provided by this invention may show great utility with various alloy systems, such as aluminum, magnesium, copper, and certain ferrous and nickel base alloys which rely on precipitation of solute for strengthening purposes. However, it is intended to be particularly useful for AA7000 series aluminum alloys of the general composition: from about 5.0 to 10.0 wt. % zinc, 1.6 to 3.2 wt. % magnesium, 1.0 to 3.0 wt. % copper, 0 to 0.15 wt. % zirconium, 0 to 0.3 wt. % titanium, chromium, hafnium, boron, or other elements added for the purpose of grain refinement, less than 0.5 wt. % Fe, Si, or other impurity elements, with the balance being aluminum. The invention is especially applicable to 7X50 type alloys such as 7050 and 7150 as well as other significantly alloyed 7000 series compositions such as 7075, 7475, and 7055. The composition ranges of these alloys are registered by the Aluminum Association Inc. in Washington, D.C. The composition of 7150 as registered with the Aluminum Association is 5.9 to 6.9 wt. % zinc, 2.0 to 2.7 wt. % magnesium, 1.9 to 2.5 wt. % copper, max. 0.12 wt. % silicon, max. 0.15 wt. % iron, max. 0.10 wt. % manganese, max. 0.04 wt. % chromium, 0.08 to 0.15 wt. % zirconium, max. 0.06 wt. % titanium, others a maximum of 0.05 wt. % each and a total of less than 0.15 wt. %, with the balance being aluminum.

The inventive two-step aging practice, due to its heating rate of less than about 100°F/hour, is not limited with respect to the type of thick product that can be produced. The invention has great utility in the aging of thick plate, extrusions, forgings or thick products of other modes of manufacture. However, in order to obtain a product which can be aged by the

inventive method, substantial processing of the product must first occur. This processing varies somewhat with respect to the product being produced, whether it is plate, extrusion, forging, etc. The specific metalworking parameters used to fabricate these various products are very well known in the art. A representative non-limiting description centered on 7000 series aluminum alloy plate processing follows.

The first step in processing involves combining the elements in the alloy by placing them in a molten state inside a furnace. The molten alloy is then fluxed by bubbling chlorine or other gases through the molten metal in order to remove hydrogen as well as impurity elements such as calcium and sodium. This "clean" metal is then poured into a mold to convert it from a liquid state to a solid mass which can then be fabricated by further operations. After the metal has solidified into a solid mass, which is typically called an ingot, it is placed in a furnace to relieve residual stresses formed during the casting operation. The stress-relieved ingot is then "scalped" which consists of sawing or machining off the rough, as-cast surface. The scalped ingot is then homogenized by heating it in a furnace to a high temperature. Alternatively, the stress relief and homogenization steps are combined. This homogenizing practice makes the chemical composition of the ingot more homogeneous by allowing the alloying elements to diffuse and be dispersed uniformly throughout the structure. For 7X50 alloys, this homogenization is typically conducted from 850°F to 900°F for 24 to 72 hours. It is important that the alloying elements be placed into solid solution to the largest extent possible. Otherwise, the intermetallic particles formed during casting, such as Al_2CuMg, will remain throughout subsequent processing and result in poor fracture toughness and fatigue properties

of the material. Following homogenization, the material is subsequently hot worked and, if necessary, cold worked to produce the shape of the desired product being produced. Although these hot working methods vary widely from rolling to extrusion to forging, they are usually accomplished in the same temperature range. For 7X50 alloys, this range is usually 800 to 700°F. Above ~810°F, the metal often loses its ductility and shatters, whereas below 700°F the stress required to deform the metal is too large and additionally the metal may recrystallize and lose toughness. Following the metalworking operation, the material is then solution heat treated in preparation for aging. Solution heat treatment involves heating the material to a high temperature to place the alloying elements into solution in the aluminum matrix. This typically occurs near the temperature of the homogenization and the time depends to an extent on the product thickness. As an example, 7X50 plate is often solutionized at 870 to 890°F for 4 to 8 hours. Immediately following solution heat treatment, the product is rapidly quenched by either immersion into a water bath or preferably by a high velocity water spray. This suspends the alloying elements in solid solution so they may be carefully precipitated during the subsequent aging process. It is this aging process which to a large extent determines the product's mechanical and corrosion properties.

The two-step inventive aging method consists of aging a solution heat treated and quenched product as follows: heating from room temperature to a high elevated temperature of about 335 to 450°F at a rate no greater than 100°F/hr. Typically rates of 20 to 50°F/hr are used. The primary reason for rates in this range is to minimize through-thickness temperature variations so as to reduce property variations in thick products. As

an example, a 6.00" thick plate of 7050 experiences only a ±1°F temperature variation when being heated at 35°F/hr. From a process control standpoint, many production furnaces presently in service in the aluminum industry can easily and accurately heat at these rates. When the high elevated temperature is reached, it is desired to hold the material at temperature for about 0.25 to 6 hours. The exact amount of time at this first step high elevated temperature can be specifically tailored for producing the final properties desired in the material. Higher temperatures and longer times promote extremely good exfoliation and stress corrosion resistance at fairly high strength. Lower temperatures and shorter times result in closer to peak strength with slightly less but still quite good corrosion resistance. The flexibility of this inventive aging method with respect to tailoring the material for specific properties will be demonstrated in detail in a subsequent example. After the material is exposed at the high elevated temperature, it is then cooled to a lower temperature in preparation for the second step age. The rate of cooling from high temperature is not considered significant. Air or water mist cooling to room temperature and then reheating to the second step lower elevated aging temperature or air cooling directly to the second step lower elevated aging temperature has not produced significant property variations. The time at the first step elevated temperature and the actual temperature itself is a more important variable in determining final material properties. Therefore, practice of this invention allows use of a cooling practice most amenable to a particular production facility.

The second, final lower elevated temperature aging step is then carried out at about 235° to 310°F for a time of about 3 to 60 hours. For 7X50 type aluminum

alloys, temperatures from 240° to 275°F for 4 to 24 hours are preferred. At lower temperatures, longer aging times are required due to the slower kinetics of precipitation. At higher temperatures, shorter times can be used because of faster aging kinetics. Although economic efficiencies can be clearly gained through the use of higher temperatures with shorter duration cycle times, it is important to note that increased production process control is also required. Additionally, if very high strength is desired, it is better to use a lower temperature, longer time second step age. This results from the fact that in almost all precipitation strengthened materials, lower isothermal aging temperatures are able to produce higher maximum achievable strengths as compared to higher aging temperatures. Following the completion of the second aging step, the material is cooled to room temperature. Usually this is best accomplished by simply removing it from the furnace.

The following examples serve to further illustrate the excellent combinations of strength, exfoliation, and stress corrosion resistance that can be obtained in 7000 series aluminum alloy products through the practice of the invention. Additionally, these examples serve to demonstrate the versatility of the inventive method so that one skilled in the art may easily and effectively practice the invention.

Example 1

At present, 7X50 thick plate is used almost exclusively in the -T7651 and -T7451 tempers primarily for increased corrosion resistance compared to -T6X type tempers. This increased corrosion resistance is unfortunately acquired at a significant decrease in strength (11 to 14 ksi compared to -T651). The goals of

this work are twofold. The primary goal is to utilize the inventive method in designing an aging practice which will produce corrosion resistance equivalent to the -T7451 temper (the most corrosion resistant temper for 7X50 alloys) but with significantly higher strength. The secondary goal is to utilize the inventive method to design an age practice which can more cost effectively produce desired -T7451 properties.

Samples from a full-size production 1.375" thick plate of 7X50-W51, the composition of which is shown in Table 1, were aged by two different two-step high-low aging practices and by -T7451 and -T651 control practices. These practices are shown in Table 2 and illustrated schematically in Figure 1. Specimens were machined from plate aged by each practice and tested as follows:

1. Tensile: duplicate 0.505" diameter round (4D) longitudinal orientation
2. Fracture Toughness (K_{1c}): duplicate W=3, L-T orientation
3. Exfoliation: duplicate tenth plane (t/10) and half thickness plane (t/2) specimens with weight loss
4. Stress Corrosion: triplicate constant strain 0.125" diameter round, ST orientation, stressed to 35 ksi for 20 days
5. Stress Corrosion: duplicate constant strain 0.125" diameter round, ST orientation, stressed to 45 ksi for 20 days

Testing was conducted in strict accordance with ASTM specifications. Table 3 summarizes the results of these tests, along with minimum specification properties for the -T651, -T7651 and -T7451 tempers for comparison purposes.

With respect to accomplishing objects of the invention, the inventive high-low two-step overaged practice (Practice #2) produced equivalent corrosion to the -T7451 temper with the added advantage of 8 ksi higher strength. More specifically, it passed stress corrosion testing at 45 ksi in the ST direction and had EA exfoliation ratings by ASTM G34-79 and ASTM G34-72 at both the tenth and half-thickness planes at a yield strength of 78.6 ksi. It is well known in the art that as strength increases, toughness decreases. Figure 2 shows that this decrease was linear in nature and therefore the inventive method additionally did not promote unexpected decreases in toughness. In short, this high-low inventive aging method produced the highest combination of strength and corrosion resistance known for thick products produced from 7X50 alloys.

Another objective of the invention, to utilize the inventive method to more cost effectively produce 7X50-T7451, was also accomplished. As can be seen in Table 3, the inventive high-low two-step heavily overaged practice (Practice #1) produced properties almost identical to the -T7451 control practice. However, it accomplished this with a 35% reduction in aging time as compared to the traditional method of producing 7X50-T7451. The energy savings associated with this reduction in aging time is significant. The reduction in aging time would have the additional advantage of increasing production aging capacity on a weight per time basis.

Example 2

In order to demonstrate the wide range of utility of the inventive aging method, an experiment was designed in order to construct a set of iso-property maps for 7X50 alloys. With the use of these maps, one skilled in the art may easily and effectively select specific times and

temperatures for the inventive high-low aging method which will result in the specific properties one desires for an application. This example is based on 7X50 alloys; however, the same experimental technique can easily be used to construct iso-property maps for other alloys such as 7X75 or 7055.

Samples from a full-size production plate of 1.00" thick 7X50-W51, the composition of which is shown in Table 4, were aged by nine different two-step high-low inventive aging practices. These practices, which are shown in Table 5, differ in only the time and temperature of their first isothermal aging step. As was stated previously, the time and temperature of the first isothermal elevated temperature step is the most important variable in producing final material properties. Therefore, in this example it is this step that has been examined with other variables, such as heating and cooling rates and second isothermal step time and temperature, being held constant.

The following specimens were machined and tested from plate aged by each practice:

1. Tensile: duplicate 0.505" diameter round (4D), longitudinal orientation
2. Exfoliation Corrosion: duplicate tenth plane (t/10) and half-thickness plane (t/2) specimens with weight loss
3. Stress Corrosion: triplicate C-ring 0.750" diameter, ST orientation, stressed to 25 ksi for 30 days
4. Stress Corrosion: triplicate C-ring 0.750" diameter, ST orientation, stressed to 35 ksi for 30 days

The results of these tests are compiled in Tables 6 and 7. These data are also presented graphically in Figures 3 through 13. Figures 3 through 13 constitute a

set of iso-property maps for 7X50. These maps show for a specific first step isothermal time and temperature the properties which will result following the completion of aging using the inventive method for the time and temperature ranges examined. One skilled in the art may easily and effectively practice the inventive method by using these maps "in reverse" to select a specific aging practice which will produce the properties one desires the material to have. As an illustration: Assume the goal is to not experience short transverse stress corrosion at a 35 ksi stress level for 30 days and have a tensile yield strength of greater than 72 ksi. One skilled in the art may superimpose the 35 ksi stress corrosion map on the yield strength map and determine the locus of aging times and temperatures which satisfy this criterion. Figure 14 shows the range of first-step isothermal times and temperatures from which one skilled in the art may select to achieve >35 ksi SCC resistance at a yield strength above 72 ksi.

This representative example serves not only to teach one skilled in the art how to easily and effectively practice the inventive aging method, but more importantly shows the wide range of utility which can be achieved through the practice of the inventive method.

In this example, the properties of the material were influenced by varying the first step of the two-step age practice. This feature of the inventive method lends itself to great flexibility and the ability to reduce costs in a plant production environment. As an illustration, assume a customer orders three plates with one set of desired properties and three plates with a different set of desired properties. A typical furnace may have a capacity of six plates or more. Using the inventive method, one can apply a different first step age separately to both types of plate, cool them to a

lower temperature, place all six plates in the same furnace, and apply an identical second step age. For this partial batch scenario just presented, the total aging time for all plates will be reduced by approximately 40%. This approximate 40% savings in thermal energy and plant aging capacity translates into a significant cost savings for producing the product using the inventive method.

It is to be understood that the above description of the present invention is susceptible to various modifications, changes, and adaptations by those skilled in the art, and that the same are to be considered to be within the spirit and scope of the inventions as set forth in the claims which follow.

Table 1

Composition of Lot #920U148A
(in wt.%)

%Zn	%Mg	%Cu	%Si	%Fe	%Ti	%Zr	%Be	%Mn	%Cr	%Ni	%Pb
6.55	2.10	2.17	0.04	0.06	0.04	0.11	<.01	<.01	<.01	<.01	<.01

Table 4

Composition of Lot #920X156C
(in wt.%)

Si	Fe	Cu	Mn	Mg	Cr	Ni	Zn	Ti	Zr	Pb
0.04	0.08	2.42	0.01	2.20	0.009	0.014	6.74	0.05	0.10	<.01

Table 2

Aging Practices

Practice #	Temper Designation	Heating Rate to 1st Isothermal Step	Temperature and Time of 1st Isothermal Step	Heating or Cooling Rate to 2nd Isothermal Step	Time and Temperature of 2nd Isothermal Step[1]	Total Calculated Aging Time[2]
1	High-Low Heavily Overaged	35°F/hr	370°F, 2 hrs	-50°F/hr	250°F, 15 hrs	27.1 hrs
2	High-Low Overaged	35°F/hr	360°F, 1.5 hrs	-50°F/hr	250°F, 15 hrs	26.1 hrs
3	-T651	35°F/hr	245°F, 24 hrs.	35°F/hr	305°F, 10 hrs	39.9 hrs
4	-T7451	35°F/hr	245°F, 8 hrs	35°F/hr	315°F, 28 hrs	42.1 hrs

[1]All samples air cooled after second isothermal step

[2]Room temperature = 100°F

TABLE 3

Temper Specifications for Comparison	(L) Tensile (ksi)	(L) Yield (ksi)	(L) % El	K_{Ic} (L-T) (ksi*in$^{1/2}$)	Uncleaned G34-79 EXCO		Cleaned G34-72 EXCO		EXCO Wt. Loss (mg/in^2)		SCC (ST) Constant E (days to failure)	
					t/10	t/2	t/10	t/2	t/10	t/2	35 ksi	45 ksi
7X50-T651 Minimum 1.001" to 1.500"	84	78	8.0	21.0	N/A*1	N/A	N/A	N/A	N/A	N/A	N/A	N/A
7050-T7651 Minimum AMS 4201B 1.000" to 1.500"	77	67	9.0	26.0	EB	N/A	EB	N/A	N/A	N/A	Above spec.*2	Above spec.*2
7050-T7451 Minimum AMS 4050E <2"	74	64	10	29.0	Plane EB	Not EB	Specified EB	EB	N/A	N/A	NF	Above Spec.
EXPERIMENTAL DATA												
7X50-T651 Control (Practice #3)	90.6	85.1	11.25	23.4	EB EB	PB PB	EB EB	EB EB	123 124	103 81	3 3 3	3 3
7X50-T7451 Control (Practice #4)	79.7	70.6	12.5	35.9	EA EA	EA EA	EA EA	EA EA	83 84	71 73	NF*3 NF NF	NF NF
7X50 Heavily overaged high-low two-step (Practice #1)	78.6	69.2	13.0	36.19	EA EA	EA EA	EA EA	EA EA	82 83	69 73	NF NF NF	NF NF
7X50 Overaged high-low two-step (Practice #2)	85.4	78.6	12.0	28.14	EA EA	EA EA	EA EA	EA EA	77 82	70 68	NF NF NF	NF NF

*1 N/A: Not applicable
*2 25 ksi minimum
*3 No failures after 20 days when tested per ASTM G44 (alternate immersion)

Table 5

Aging Practices for Construction of 7X50 Iso-Property Maps

Practice #	Heating Rate to 1st Isothermal Step (°F/hr.)	1st Isothermal*1 Step Time (min.)	1st Isothermal*1 Step Temperature (°F)	Heating Rate to 2nd Isothermal Step (°F/hr.)	2nd Isothermal*2 Step Time (hrs.)	2nd Isothermal*2 Step Temperature (°F)
1	25	90	340	25	13.5	250
2	25	90	350	25	13.5	250
3	25	90	365	25	13.5	250
4	25	60	340	25	13.5	250
5	25	60	350	25	13.5	250
6	25	60	365	25	13.5	250
7	25	120	340	25	13.5	250
8	25	120	350	25	13.5	250
9	25	120	365	25	13.5	250

*1: Removed from furnace and air cooled after this first isothermal step

*2: All specimens batch aged together during the second isothermal step and then removed from furnace and air cooled after completion of aging

Table 6

Tensile and Exfoliation Corrosion Properties of 7X50 After Aging by the 9 Practices Defined in Table 5

Practice Number	(L) Tensile (ksi)	(L) Yield (ksi)	(L) % Elongation	Exfoliation ASTM G34-79		Exfoliation ASTM G34-72		Exfoliation Wt. Loss (mg/in^2)	
				t/10	t/2	t/10	t/2	t/10	t/2
1	88.35	84.06	11.25	EA	EB	EA	EA	146.0	238.0
2	85.29	79.75	12.0	EA	EA	EA	PB	101.5	107.0
3	78.44	69.74	13.5	EA	EA	EA	PB	104.5	106.5
4	89.45	85.49	11.0	EA	ED	EA	EC	272.0	412.5
5	87.20	82.79	11.0	EA	EA	EA	EA	117.0	112.0
6	81.10	73.69	13.0	EA	EB	EA	EA	115.0	81.0
7	87.71	82.98	11.5	EA	EB	EA	EA	139.5	143.5
8	85.47	79.86	11.75	EA	EB	EA	EA	95.5	85.5
9	77.63	68.58	14.75	EA	EB	EA	EA	108.0	86.0

Table 7

Stress Corrosion Properties of 7X50 After Aging by the 9 Practices Defined in Table 5

Practice Number	Stress Corrosion 25 ksi		Stress Corrosion 35 ksi	
	Days No Failure	Days to Failure	Days No Failure	Days to Failure
1	--	11, 11, 30	--	2, 2, 14
2	30, 30, 30	--	30, 30, 30	--
3	30, 30, 30	--	30, 30, 30	--
4	--	2, 2, 2	--	2, 2, 2
5	30	30, 30	--	30, 30, 30
6	30, 30, 30	--	30, 30, 30	--
7	30, 30	30	--	30, 30, 30
8	30, 30, 30	--	30, 30, 30	--
9	30, 30, 30	--	30, 30, 30	--

What is Claimed is:

1. A method for producing a thick aluminum alloy product with enhanced combinations of strength, exfoliation corrosion resistance, and stress corrosion resistance which comprises:

(a) providing an aluminum-base alloy comprising from about: 5.0 to 10.0 wt.% zinc, 1.6 to 3.2 wt.% magnesium, 1.0 to 3.0 wt.% copper, 0 to 0.15 wt.% zirconium, 0 to 0.3 wt.% of at least one of titanium, chromium, hafnium, boron, and other elements added for the purpose of grain refinement, less than 0.5 wt.% iron, silicon and other impurity elements, with the balance being aluminum;

(b) working the alloy into a thick aluminum alloy product;

(c) solution heat treating the product;

(d) quenching the heat treated product;

(e) stretching the quenched product to improve flatness and reduce residual stresses; and

(f) aging the thick aluminum alloy product by an aging process of: heating the product from about room temperature at one or several rates all of which are less than about 100°F/hr. to a first high elevated

temperature step of about 335°F to 450°F holding the product at the first step for a time of about 0.25 to 6 hours, and holding the product at a lower elevated temperature step of about 235°F to 310°F for a time of about 3 to 60 hours to thereby produce a thick aluminum alloy product with enhanced combinations of strength, exfoliation corrosion resistance, and stress corrosion resistance.

2. The method of Claim 1 wherein the heating from about room temperature to the first high elevated temperature step is between 15°F/hr. and 50°F/hr.

3. The method of Claim 1 wherein the first high elevated temperature step consists of one or more temperatures within about 340°F to 365°F.

4. The method of Claim 1 wherein the lower elevated temperature step consists of one or more temperatures within about 240°F to 270°F.

5. The method of Claim 1 wherein the aluminum alloy product is cooled directly from the first high elevated temperature step to the lower elevated temperature step.

6. The method of Claim 1 wherein the aluminum alloy product is cooled from the first high elevated temperature step to a temperature below the lower elevated temperature step and then reheated for subsequent aging at the lower elevated temperature step.

7. The method of Claim 1 wherein the aluminum alloy is a 7X75 alloy.

8. The method of Claim 1 wherein the aluminum alloy is a 7055 alloy.

9. A method for producing a thick aluminum alloy product with improved combinations of strength, exfoliation corrosion resistance, and stress corrosion resistance which comprises:

(a) providing an aluminum-base alloy consisting essentially of from 5.7 to 6.9 wt.% zinc, 1.9 to 2.7 wt.% magnesium, 1.9 to 2.6 wt.% copper, about 0.08 to 0.15 wt.% zirconium, 0 to 0.3 wt.% of at least one of titanium, chromium, hafnium, boron, and other elements added for the purpose of grain refinement, balance aluminum and incidental impurities;

(b) working the alloy into a thick product;

(c) solution heat treating the thick product;

(d) quenching the heat treated thick product;

(e) stretching the quenched thick product to improve flatness and reduce residual stresses;

(f) aging by an aging process which includes heating the thick product from about room temperature at one or several rates all of which are less than about 100°F/hr. to

a first high elevated temperature step of about 335°F to 450°F holding the thick product at the first step for a time of about 0.25 to 6 hours, holding the thick product at a second, a lower elevated temperature step of about 235°F to 310°F for a time of about 3 to 60 hours.

10. The method of Claim 9 wherein the heating from about room temperature to the first high elevated temperature is between 15°F/hr. and 50°F/hr.

11. The method of Claim 9 wherein the first high elevated temperature step consists of one or more temperatures within about 340°F to 365°F.

12. The method of Claim 9 wherein the second elevated temperature step consists of one or more temperatures within about 240°F to 270°F.

13. The method of Claim 9 wherein the aluminum alloy product is cooled directly from the first high elevated temperature step to the second elevated temperature step.

14. The method of Claim 9 wherein the aluminum alloy product is cooled from the first high elevated temperature step to a temperature below the second elevated temperature step and then reheated for subsequent aging at the second elevated temperature step.

15. The product of Claim 9 wherein the alloy has a yield strength greater than 64 ksi and stress

corrosion resistance of greater than 35 ksi when tested in the short transverse orientation.

16. The product of Claim 9 wherein the alloy has a yield strength greater than 67 ksi and a stress corrosion resistance of greater than 25 ksi when tested in the short transverse orientation.

17. The product of Claim 1.

18. The product of Claim 2.

19. The product of Claim 3.

20. The product of Claim 4.

21. The product of Claim 5.

22. The product of Claim 6.

23. The product of Claim 7.

24. The product of Claim 8.

25. The product of Claim 9.

26. The product of Claim 10.

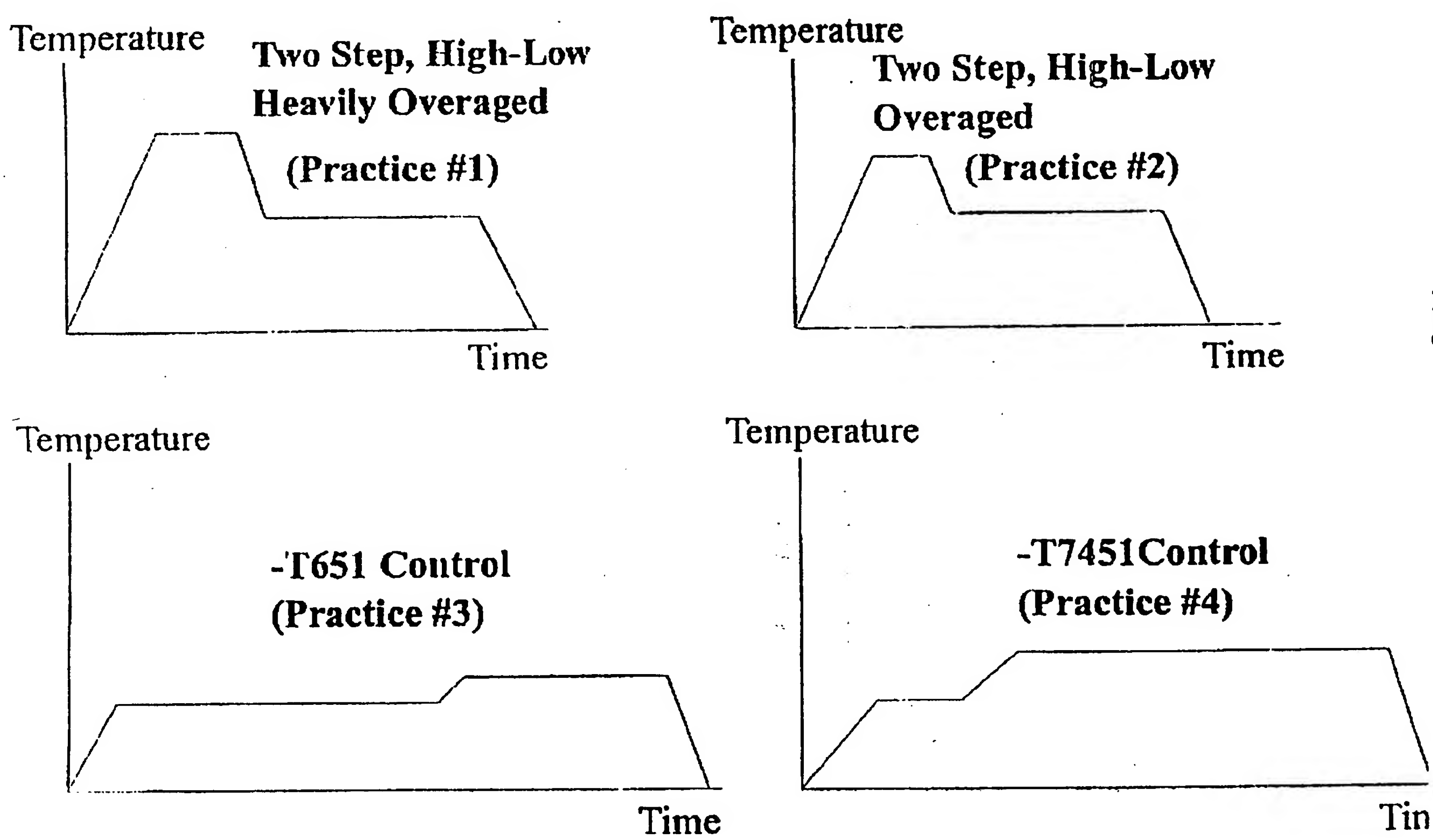
27. The product of Claim 11.

28. The product of Claim 12.

29. The product of Claim 13.

30. The product of Claim 14.

Schematic of Aging Practices



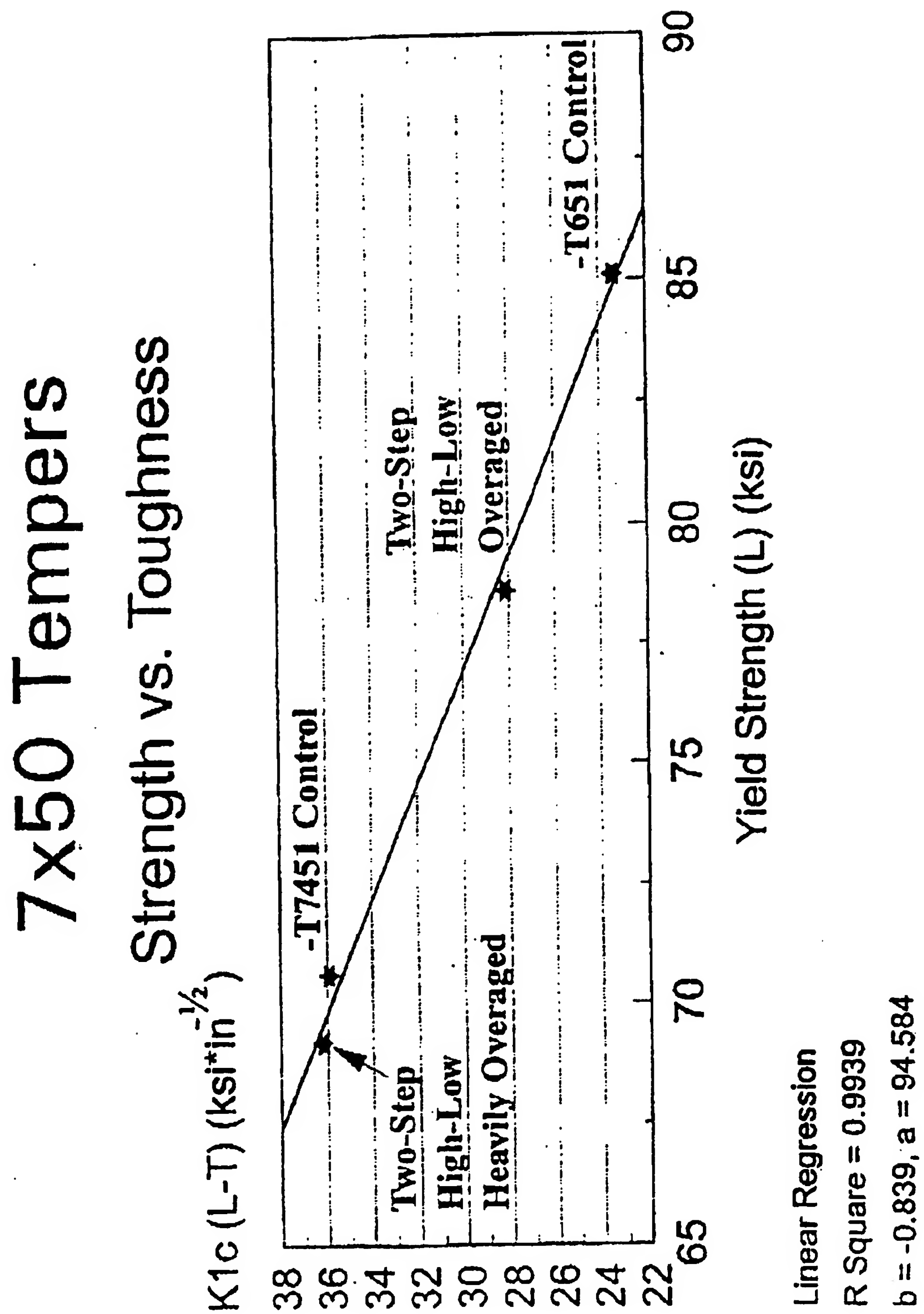

7x50 Tempers
Strength vs. Toughness
K1c (L-T) (ksi*in^-½)
38
36
34
32
30
28
26
24
22
65
70
75
80
85
90
Yield Strength (L) (ksi)
-T7451 Control
Two-Step
High-Low
Heavily Overaged
Two-Step
High-Low
Overaged
-T651 Control
Linear Regression
R Square = 0.9939
b = -0.839, a = 94.584

Figure 4

Longitudinal Ultimate Tensile Strength (ksi)
(0.505" dia. round, 4D specimens)
Lot # 920X156C

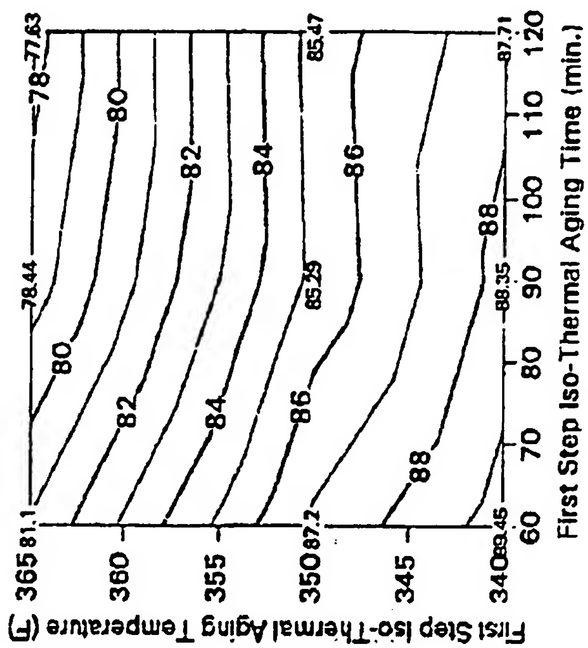


Figure 3

Longitudinal Tensile Yield Strength (ksi)
(0.505" dia. round, 4D specimens)
Lot# 920X156C

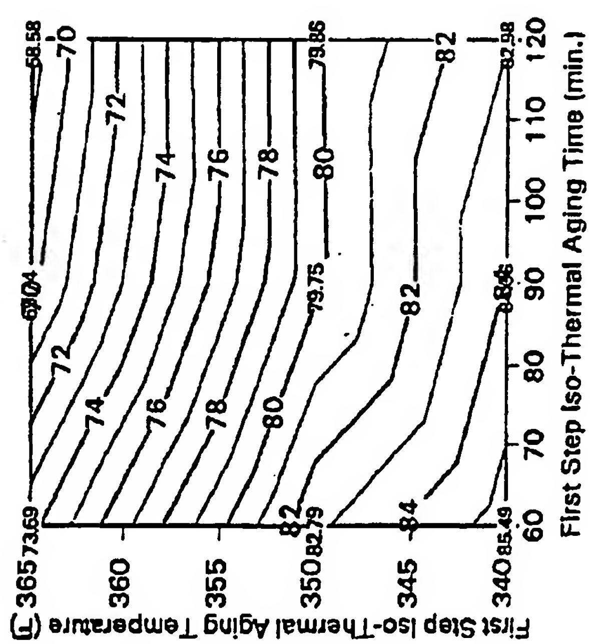


Figure 5

% Tensile Elongation
(0.505" dia. round, 4D specimens)
Lot# 920X156C

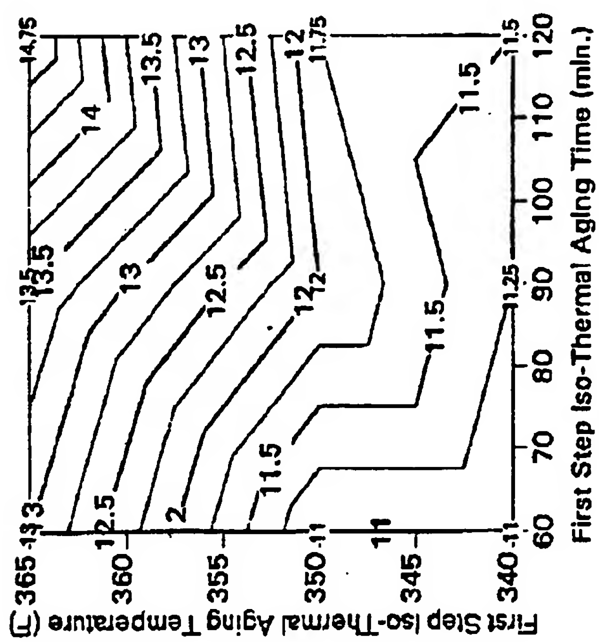
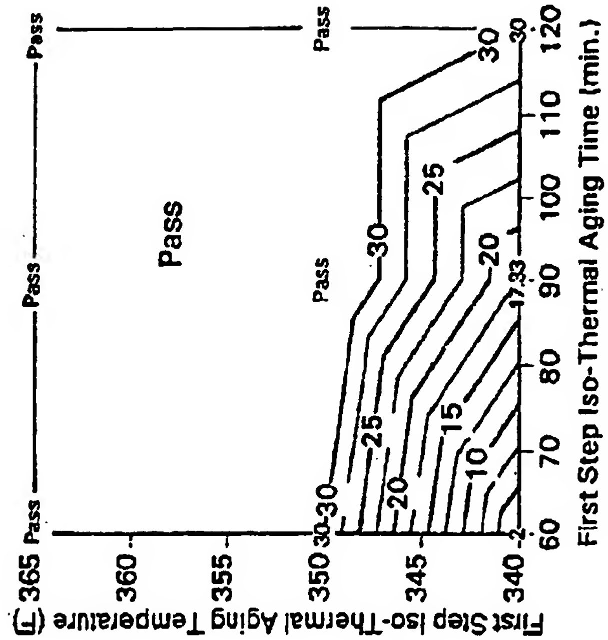


Figure 6

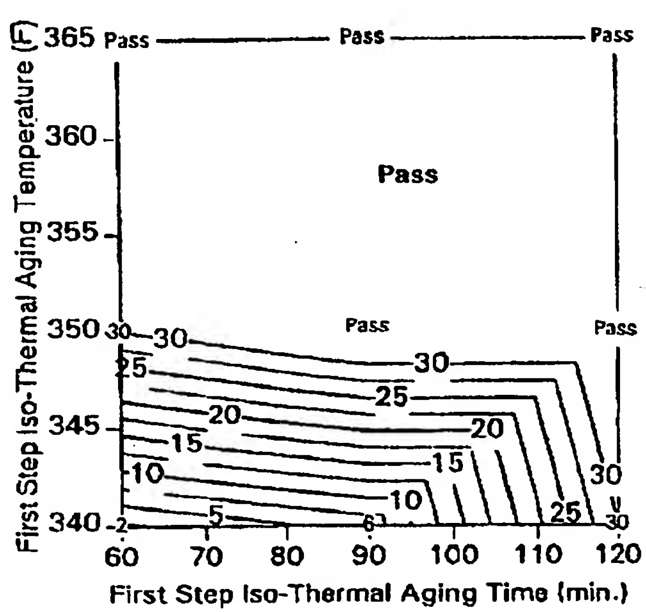
Short Transverse Stress Corrosion
C-Ring Samples at 25 Ksi
Days to Failure of Failed Samples*
Lot# 920X156C



* Triplicate Samples. Example: Pass, 25 days, 30 days = 27.5 day failure.

Figure 7

Short Transverse Stress Corrosion
C-Ring Samples at 35 Ksi
Days to Failure of Failed Samples*
Lot# 920X156C



* Triplicate Samples. Example: Pass, 25 days, 30 days = 27.5 day failure.

Figure 8

Exfoliation Corrosion Resistance
ASTM G34-79 (uncleaned method)
t/10 Thickness Plane
Lot# 920X156C

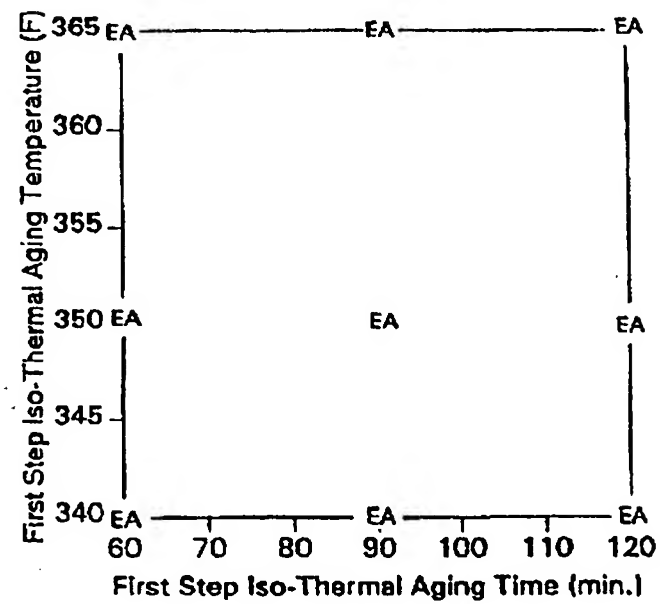


Figure 9

Exfoliation Corrosion Resistance
ASTM G34-72 (cleaned method)
t/10 Thickness Plane
Lot# 920X156C

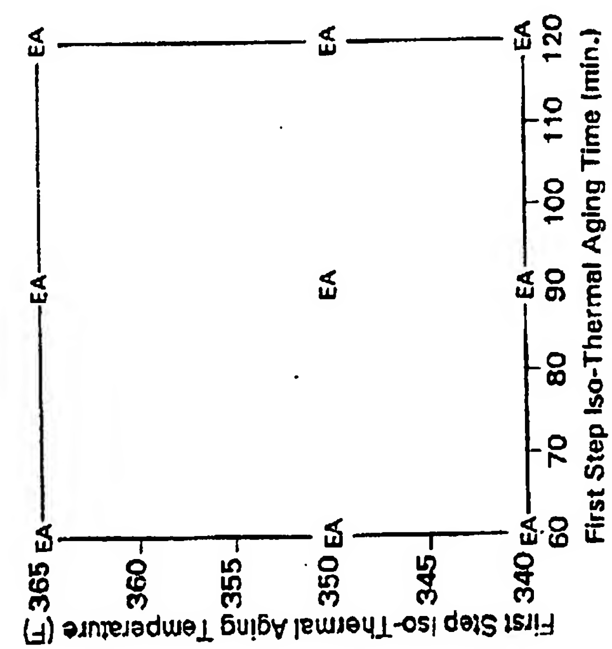


Figure 10

Exfoliation Corrosion Resistance
ASTM G34-79 (uncleaned method)
t/2 Thickness Plane
Lot# 920X156C

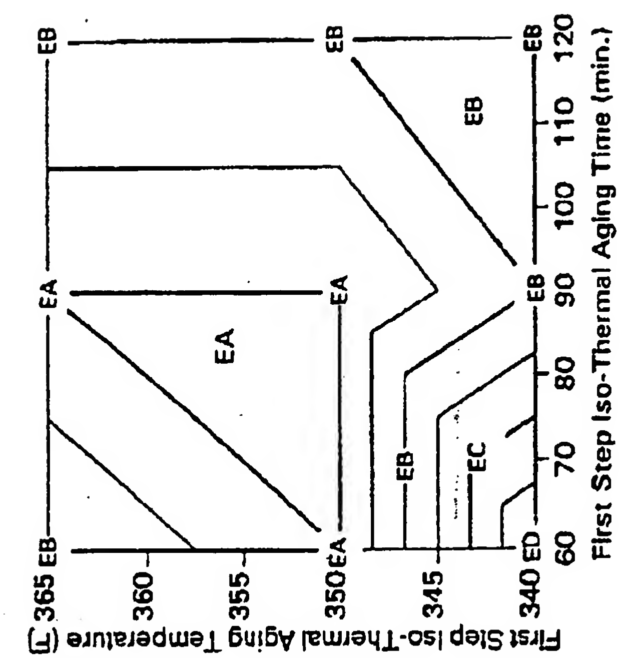


Figure 11

Exfoliation Corrosion Resistance
ASTM G34-72 (cleaned method)
t/2 Thickness Plane
Lot# 920X156C

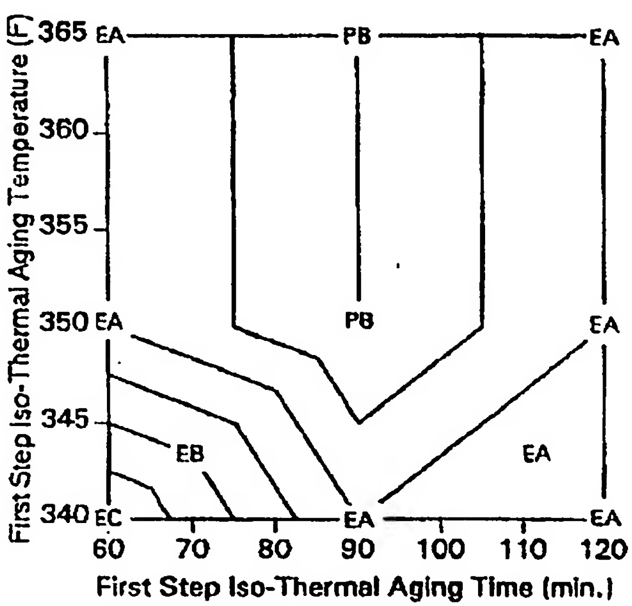


Figure 12

Exfoliation Corrosion Weight Loss
t/10 Thickness Plane
(mg/in^2)
Lot# 920X156C

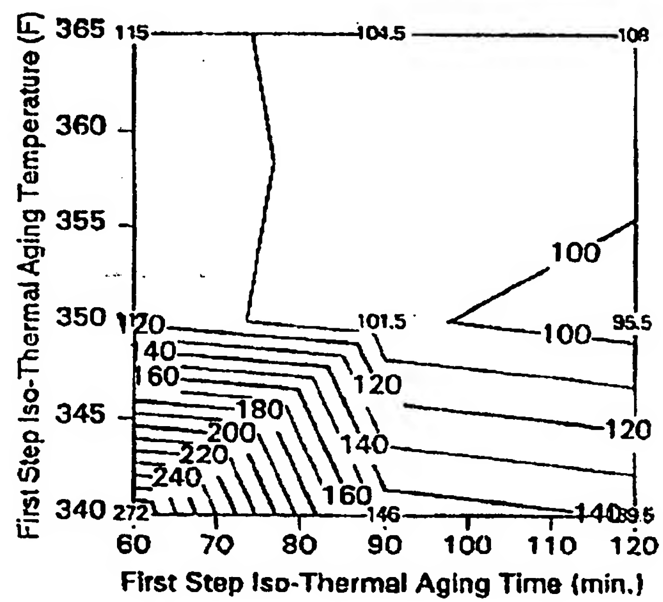


Figure 14

Example of Superposition of Yield Strength and 35 Ksi Stress Corrosion Iso-Property Maps (for >72 ksi and >30 days)

Lot# 920X156C

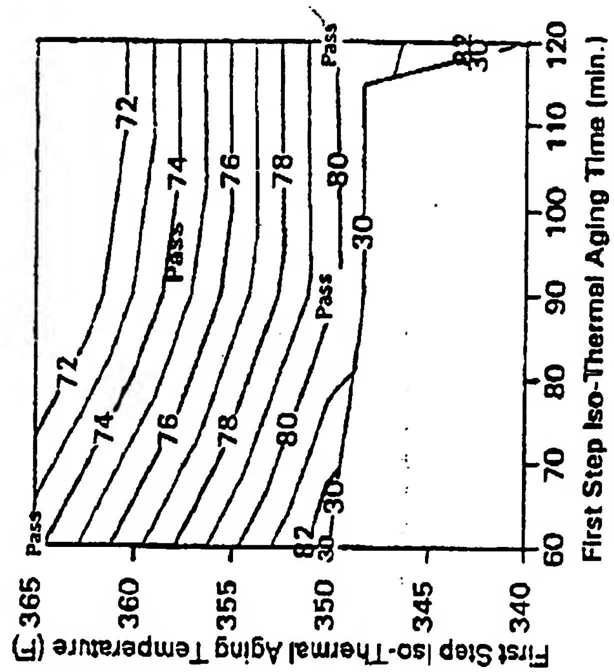
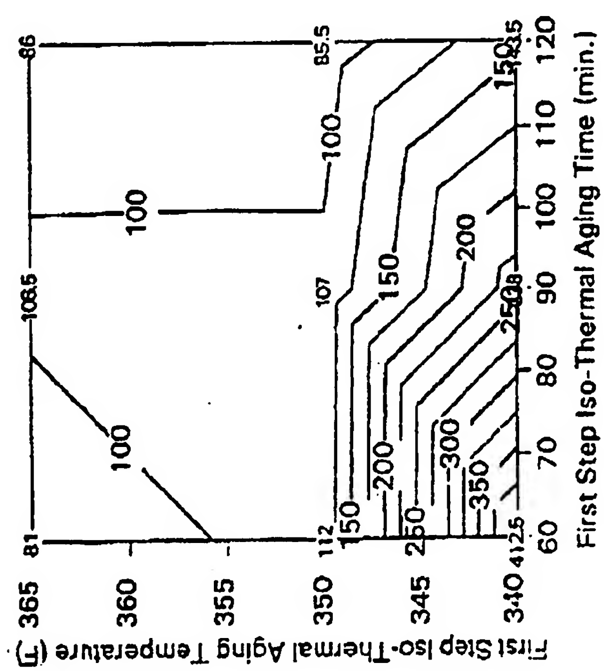


Figure 13

Exfoliation Corrosion Weight Loss t/2 Thickness Plane (mg/in^2)

Lot# 920X156C



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US95/02705

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :C22F 1/04
US CL :148/694, 697, 701, 417, 439
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 148/694, 697, 701, 417, 439

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

None

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

None

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US, A, 3,305,410 (SUBLETT ET AL) 21 February 1967, col. 1, line 49 to col. 2, line 23; col. 2, lines 52 to 58; and col. 4, line 63 to col. 5, line 40 (including Table 4).	1-30
Y	US, A, 3,881,966 (STALEY ET AL) 06 May 1975, col. 2, line 14 to col. 3, line 21.	1-30
Y	TRANSACTIONS OF THE METALLURGICAL SOCIETY OF AIME, Volume 245, issued September 1969, R.F. Ashton et al, "Effect of Heating Rate on the Aging Behavior of 7075 Alloy", pages 2101-2102.	1-30

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search
01 JUNE 1995

Date of mailing of the international search report
28 JUN 1995

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